# GOLF BALL WITH CO-INJECTED COVER

## CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of co-pending U.S. Application No. 10/641,747 that was filed on August 15, 2003, which was a divisional of U.S. Application No. 10/055,232 which was filed January 23, 2002 and is now U.S. Patent No. 6,676,541, and is incorporated herein in its entirety by express reference thereto.

## FIELD OF INVENTION

The invention relates generally to golf balls, and more specifically, to a multi-layered golf ball having three cover layers that are co-injection molded. At least one of the cover layers comprises a foaming agent.

## BACKGROUND OF THE INVENTION

It is well known that golf balls are typically constructed with a cover that tightly surrounds a core. It is typical for a golf ball core to have a solid construction or a wound construction and the methods of forming these cores are well known in the art. Traditionally, golf ball covers are formed from polymeric materials. For instance, golf balls have traditionally incorporated covers made of balata rubber, which may be a natural balata, a synthetic balata, or a blend of natural and synthetic balata.

Other golf balls have incorporated covers which are formed from synthetic polymeric materials such as polyolefins and in particular, polyethylene, polyurethanes, and ionic copolymers of olefins. The latter mentioned ionic copolymers of olefins were commercially introduced in the mid 1960's by E. I. Du Pont de Nemours & Co., Inc., Wilmington, Del. (DuPont) and sold under the trademark "SURLYN." Golf balls incorporating SURLYN covers are generally

described in U.S. Pat. No. 3,454,280. Cover compositions that are based on SURLYN resins are advantageous in that the resulting covers are cut and abrasion resistant compared to the balata covers. While golf balls incorporating SURLYN resin covers are commonly known by players to be more cut resistant than balata covered balls, they traditionally tend to reduce the spin imparted to a golf ball and produce a less desirable "feel" as compared to a balata covered ball.

SURLYN resins sold by DuPont typically contain zinc, lithium, magnesium or sodium ions. A number of SURLYN resins, of varying physical properties, are sold by DuPont. The physical properties of these resins are described in technical bulletins that are readily available from DuPont. Mixtures of various SURLYN resins as cover stock materials are likewise highly advantageous. Suitable mixtures for use as cover materials are described in U.S. Pat. No. 3,819,768.

For purposes of control, golfers strike a golf ball in such a manner that the ball has substantial backspin. It is desirable that a golfer be able to impart backspin to a golf ball for purposes of controlling its flight and controlling the action of the ball upon landing on the ground. For example, substantial backspin will make the ball stop once it strikes the landing surface instead of bounding forward. The ability to impart back spin onto a golf ball is related to the deformation of the golf ball cover when struck with a golf club. Generally, the more deformable the cover is, the easier it is to impart spin to the balls. This is particularly true for short or wedge shots.

Thus, it is desirable to combine the properties of SURLYN covered golf balls with the properties of Balata covered golf balls. For example it is desirable to have less spin on a drive, such that the ball will have a "low spin trajectory". The result is that the ball does not climb like a typical high spin rate ball would, and the ball has substantial roll after it lands on the ground to provide maximum distance. On the other hand, for approach shots, i.e., short shots into the green, spin is critical to control the ball when it lands. With a high spin rate, the ball will stop or "sit" when it hits the green. Thus, with a high spin rate, the ball can be hit directly at the target. With a low spin rate, the ball often bounces off the green or "runs" off the green.

Thus, it is desirable to have a high spin rate for approach shots into the green.

Further, it is desirable to combine the durability of SURLYN covered balls with the characteristics of balata covered balls.

Typically, the golf ball cover layer is formed by one of two processes. The first process includes the compression molding of hemispheres. First, two hemispherical covers, called half-shells, are injection molded. The hemispheres are then placed around a core and compression molded so that they fuse around the core and wherein dimples are imparted into the cover. The cover is then finished to remove any visible molding lines or residue. The second process, called the retractable pin injection molding process, involves injection molding of the cover directly around a core positioned on pins, removing the pins once the cover material surrounds the core, removing the covered core, and finishing it to form a completed golf ball. In both cover forming processes, the injection molding of the covers involves techniques known in the art. These techniques generally involve forcing molten material to substantially fill and take on the shape of a mold, thereby forming a cover or hemisphere. When the material is cool enough to substantially maintain the shape of the mold, it is ejected from the mold.

Typically, the cover material begins the injection molding process as resin pellets that are stored in a hopper. The pellets are gravity fed into a heated cylinder that melts the pellets as a screw simultaneously pushes the softening pellets toward an accumulation zone. When enough molten material is accumulated to fill the mold, the screw is pushed or stroked forward, thereby forcing the melted material into the mold. Many prior art references are directed to mixing different materials to form new cover materials. This is traditionally accomplished by mixing pellets of different materials in the injection mold machine hopper.

There are also many patents that are directed to golf balls having multiple cover layers. For example, U.S. Pat. No. 4,431,193 relates to a golf ball having a multilayer cover wherein the inner layer is a hard, high flexural modulus ionomer resin and the outer layer is a soft, low flexural modulus ionomer resin, and wherein either or both

layers may comprise a foamed ionomer resin.

U.S. Pat. No. 5,314,187 also relates to golf balls having multiple layer covers, wherein the outer layer is molded over the inner layer and comprises a blend of balata and an elastomer where the inner layer is an ionomer resin.

U.S. Pat. No. 4,919,434 is directed towards a golf ball having a cover which comprises an inner layer and an outer layer each of which is a thermoplastic resin. Preferably the layers comprise thermoplastic resin materials that are capable of fusion bonding with each other.

U.S. Pat. No. 5,783,293 discloses a golf ball with a multi-layered cover formed by a co-injection molding process, wherein the golf ball cover comprises an inner and outer layer of a first material and an intermediate layer therebetween of a second material.

## SUMMARY OF THE INVENTION

The present invention relates to golf balls having a cover formed by co-injection molding. One embodiment of the present invention provides for the cover to consist of three thin layers, an inner layer, an outer layer and an intermediate layer sandwiched between the other layers. The cover is formed by a co-injection molded process as disclosed in U.S. Patent No. 5,783,293, which is incorporated by reference herein in its entirety. In a preferred embodiment, the resulting golf ball has at least one of the thin layers containing a foamed material for a wound core or dual layered, solid core ball.

Another embodiment of the invention provides for only the outer and inner layers of the outer cover to comprise foamed material. The outer and inner layers comprised of a different material than the intermediate layer.

An additional embodiment of the invention provides for the intermediate layer to comprise of the foamed material, with the material of the inner and outer layers having different physical properties than that of the intermediate layer.

Still another embodiment of the invention provides for all three layers, outer, inner and intermediate, to be of the same material with either the inner and outer layers, or the intermediate layer having the foamed material.

`The cover layer is as thin as 0.005 inches and consist of a sandwich configuration. The manipulation of layer thickness and material selection effects the density, hardness, COR, etc. greatly effects ball performance.

The use of thin multi-layers, in combination with gravity adjusting materials creates moment of inertia gradients across the cover layers.

The present invention is also directed towards a golf ball having a multi-layer cover formed by a co-injection molding process, whereby a first material is divided into an inner layer and an outer layer by an injected intermediate layer of a second material. More particularly, the inner and outer layers are preferably thinner than the intermediate layer. The intermediate layer is preferably about 2/5 to 4/5 of the cover thickness and the outer layer is less than about 1/5 of the cover thickness.

The cover materials each may be a dynamically vulcanized thermoplastic elastomer, a functionalized styrene-butadiene elastomer, a polyetherester, a polyesterester, a metallocene polymer, a thermoplastic polyetheramide, a thermoplastic ionomer, a thermoplastic polyester, a thermoplastic polyurethane, a ethylene or propylene based polymer, a methyl acrylate, a methyl methacrylate polymer, a polycarbonate, a polyamide, a polyphenylene oxide, a polyether ketone, a polysulfone, an acrylonitrile butadiene polymer, an acrylic styrene-acrylonitrile polymer, a terphthalate polymer, an ethylenevinyl alcohol polymer, a tetrafluoroethylene polymer, a reinforced polymer, or blends thereof.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a golf ball according to an embodiment of the present invention disclosing a dual cover, with the inner cover consisting of three thin layers of two different materials formed by a co-injection molding process.

FIG. 2 is a golf ball according to FIG. 1, wherein the outer cover consists of three thin layers formed by a co-injection process.

FIG. 3 is a ball cover hemisphere.

FIG. 4 is a golf ball wherein both the inner cover and outer covers consist of three thin layers of two different materials and are formed by a co-injection process.

FIG. 5 is an elevational sectional view of a multi-material injection molding machine for making ball cover hemispheres.

FIG. 6 is an enlarged section of FIG. 5 showing the plunger completing the injection of material to form a cover hemisphere.

FIG. 7 is an enlarged section of FIG. 5 showing the plunger completing the injection of material to form a cover hemisphere.

FIG. 8 is an enlarged section of FIG. 5 showing the mold three-way valve.

FIG. 9 is an enlarged section of FIG. 5 showing the mold three-way valve.

FIG. 10 is an elevational sectional view of a multi-material injection molding machine for making ball cover hemispheres having a hot runner system.

## DETAILED DESCRIPTION OF THE INVENTION

Referring to FIGS. 1, 2 and 4, a golf ball **20** having a core **21**, an inner cover **22** and an outer cover **23** is shown. FIG. 1 shows the inner cover **22** consisting of three thin layers **24, 25** and **26** formed by a co-injection molding machine and process as described in Patent No. 5,783,293. This process employs a sandwich injection molding machine **40**, as shown in FIG. 5, and produces a two-material, golf ball cover hemisphere **30**, as depicted in FIG. 3. The layers **24, 25** and **26** are as thin as 0.005 inches and the resulting golf ball **20** will have four cover layers and a total of five layers for a solid core ball and six total layers for a wound core or dual core ball. FIG. 2 describes the outer cover **23** having three thin layers **27, 28** and **29** formed by the co-injection process. FIG. 4 illustrates the golf ball **20** having both covers **22** and **23**

each consisting of the three co-injection molded layers **24**, **25**, **26** and **27**, **28**, **29** respectively. This provides for a ball having six cover layers and a total of seven layers for a solid core ball and eight total layers for a wound core or dual core ball. The manipulation of layer thickness and material selection greatly effects the hardness, COR, and moment of inertia which subsequently effects ball performance. The use of gravity adjusting materials, moisture barriers and hardness gradients will be discussed later.

Referring to FIG. 5, a sandwich injection-molding machine **40** for producing a golf ball cover hemisphere **30** having two-materials is shown. The injection molding machine **40** includes two hoppers **41** and **42**, an accumulation chamber **43**, a mold **44**, a three-way valve **45**, and a plurality of channels **46**, **47** and **48** interconnecting the same. More particularly, a first hopper **41** contains a first material **31** and a second hopper **42** contains a second material **32**. The three-way valve **45** controls the flow direction of the materials **31** and **32**. The first channel **46** connects the first hopper **41** with the three-way valve **45**. The second channel **47** connects the accumulation chamber **43** to the three-way valve **45**. The third channel **48** connects the three-way valve **45** with the mold cavity **50**.

The process comprises the steps of, pellets of a first material **31** being loaded into hopper **41**, where they feed by gravity or other means known in the art to screw **51**. Then heat is applied to plasticize the first material **31** and screw **51** turns within cylinder **52** to pump a measured amount of plasticized first material **31** through channel **46** to the three-way valve **45**. The material is heated above its melt temperature and preferably to a temperature greater than about 400°F. The three-way valve **45** is positioned such that the flow of the molten first material **31** is fed into the accumulation chamber **43**. The accumulation chamber **43** is heated such that the material remains in the molten state. Next, the valve **45** selectively permits material flow from channel **46** into accumulation chamber **43** (see FIG. 8); and material flow from accumulation chamber **43** to mold cavity **50** without diversion back into channel **46** (see FIG. 9). Pellets of a second material **32** are then loaded into hopper **42**,

where they feed by gravity or other means known in the art to screw **53**. Heat is then applied to plasticize the second material **32**. The material is heated above its melt temperature and preferably to a temperature greater than about 400°F. Screw **53** forces a measured amount of plasticized second material **32** into accumulation chamber **43**, where the second material **32** and the first material **31** are juxtaposed.

The first step of the process includes inserting a predetermined amount of the second material **32** into the heated accumulation chamber **43** with the three-way valve **45** closed. Then a predetermined amount of the first material **31** is inserted into the accumulation chamber **43** through the three-way valve 45 as shown in FIG. 8. Thereafter, the position of three-way valve **45** is changed, such that the flow path to channel **46** is closed, and the flow path through passageway **48** to the mold cavity **50** is open. A plunger **54** is used to force both the first material **31** and the second material **31** past three-way valve **45**, through channel **48** and into the mold cavity **50**. The mold cavity **50** is substantially in the shape of a hemispherical half-shell, and is formed by a mold half **55** and a mold half **56**.

Turning to FIG. 6, plunger **54** is translated to the left, pushing materials **31** and **32** through valve **45** along channel **48** into mold cavity **50**. At this point, only the first material **31** has entered the mold cavity **50**. The flow is circumferential about the channel **48**. The mold halves **55** and **56** are cooled so that the molten material solidifies in the mold cavity **50**. Preferably, the mold halves **55** and **56** are maintained at a temperature below about 100°F. Most preferably, the mold halves are maintained at a temperature below 50°F so that the molten material freezes to the mold walls **57** and **58**. First material **31**, thus, flows into the mold cavity **50** and substantially adheres to the cavity surfaces **57** and **58** of mold cavity **50**. Since there is a sharp temperature gradient in the first material **31**, hot in the center and cold on the edges against the mold halves **55** and **56**, the flow of material is much easier through the center. The material must be pushed into the mold cavity **50** with sufficient pressure to allow the material to fill the cavity 50 before it solidifies.

Referring now to FIG. 7, second material **32** with the first material **31**

substantially fills the mold cavity **50**. The second material **23** follows the first material **31**. The mold **44** is maintained at a temperature much lower than the melting temperature of the first material **31**, generally a temperature of less than 100°F, and preferably about 50°F. Because of this the first material **31** solidifies against the surfaces **57** and **58** of the mold cavity **50** as it flows into the mold cavity **50**. Flow into the mold cavity **50** is, thus, through the middle or center of the first material **31**. Since the second material **32** follows the first material **31**, it flows through the center of the inner and outer layers **24** and **26**, forming an intermediate layer **25** (see FIG. 3). In order to increase the thickness of the inner and outer layers **24** and **26**, more first material **31** can be used and the flow rate into the mold decreased. To make thinner inner and outer layers **24** and **26**, less first material **31** is used and the flow rate into the mold increased. Preferably, the intermediate layer **25** comprises about 2/5 to 4/5 of the cover thickness with the outer layer **26** comprising about 1/5 or less of the thickness.

Once the materials **31** and **32** cool enough to substantially retain the shape of the mold cavity, the mold halves **55** and **56** are separated, and an ejector **61** (see FIG. 5) ejects a two material, three-layer hemisphere **30** (see in FIG. 3) from the injection molding machine **40**.

Referring to FIG. 1, a completed golf ball **20** according to the present invention is shown. Core **21** is surrounded by the inner cover **22** which is comprised of two three-layer hemispheres **30** which have been compression molded together, thereby forming compression molding seam **60**. Compression molding hemispheres onto a core generally involves applying pressure and heat to mold the cover hemispheres onto the core and is known in the art. It is contemplated that the core **21** is a solid, polybutadiene type core, a solid core having multiple layers or a wound core.

It is contemplated that first material **31** and second material **32** each comprise one or more polymers. Useful polymers include a thermoplastic ionomer, a dynamically vulcanized thermoplastic elastomer, a functionalized styrene-butadiene elastomer, a polyetherester, a polyesterester, a metallocene polymer, a thermoplastic

polyetheramide, a thermoplastic polyester, a thermoplastic polyurethane, an ethylene or propylene based polymer, a methyl acrylate, a methyl methacrylate polymer, a polycarbonate, a polyamide, a polyphenylene oxide, a polyether ketone, a polysulfone, an acrylonitrile butadiene polymer, an acrylic styrene-acrylonitrile polymer, a terphthalate polymer, an ethylenevinyl alcohol polymer, a tetrafluoroethylene polymer, a reinforced polymer, or blends thereof. As noted above, the first and second layers should be different polymers or be polymers that have different properties.

Most preferably the first material **31** and second material **32** are comprised of thermoplastic ionomers or of a balata rubber and a thermoplastic ionomer, respectively. Suitable thermoplastic ionomer resins include any number of olefinic based ionomers including SURLYN® and IOTEK®, which are commercially available from DuPont and Exxon, respectively.

Among the preferred materials for first material **31** and/or second material **32** are ionomer resins obtained by providing a cross metallic bond to polymers of monoolefin with at least one member selected from the group consisting of unsaturated mono- or di-carboxylic acids having 3 to 12 carbon atoms and esters thereof (the polymer contains 1 to 50% by weight of the unsaturated mono- or di-carboxylic acid and/or ester thereof). More particularly, such acid-containing ethylene copolymer ionomer component of the subject invention includes E/X/Y copolymers where E is ethylene, X is a softening comonomer such as an acrylate, e.g., methyl acrylate, iso-butyl acrylate or n-butyl acrylate, present in 1-60 (preferably 10-40, most preferably 10-25), weight percent of the polymer, and Y is ethylenically unsaturated organic acid, such as acrylic or methacrylic acid, present in 5-35 (preferably 10-35, most preferably 10-21) weight percent of the polymer, wherein the acid moiety is neutralized 1-90% (preferably at least 40%, most preferably at least about 60%) to form an ionomer by a cation such as lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc or aluminum, or a combination of such cations. Lithium, sodium, magnesium and/or zinc are preferred.

Specific acid-containing ethylene copolymers include ethylene/acrylic acid, ethylene/methacrylic acid, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/n-butyl acrylate, ethylene/methacrylic acid/iso-butyl acrylate, ethylene/acrylic acid/iso-butyl acrylate, ethylene/methacrylic acid/n-butyl methacrylate, ethylene/acrylic acid/methyl methacrylate, ethylene/acrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl methacrylate, and ethylene/acrylic acid/n-butyl methacrylate. Preferred acid-containing ethylene copolymers include ethylene/methacrylic acid, ethylene/acrylic acid, ethylene/methacrylic acid/n-butyl acrylate, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/methyl acrylate and ethylene/acrylic acid/methyl acrylate copolymers. The most preferred acid-containing ethylene copolymers are ethylene/methacrylic acid, ethylene/acrylic acid, ethylene/(meth)acrylic acid/n-butyl acrylate, ethylene/(meth)acrylic acid/ethyl acrylate, and ethylene/(meth)acrylic acid/methyl acrylate copolymers.

The manner in which the ionomers are made is well known in the art as described, e.g., in U.S. Pat. No. 3,262,272. Such ionomer resins are commercially available from DuPont Co. under the trade name SURLYN®.

Additionally, foamed polymeric materials, in particular, metallocene-based foam resins are suitable for use in the cover layers of the present invention.

Still further, the first or second materials **31** or **32** can be comprised of balata rubber or of a synthetic balata.

In the present invention, first material **31** has a melting point or heat of reaction (cure) temperature that is similar to that of second material **32**. Alternatively, first material **31** has a melting point or heat of reaction temperature that is higher than that of second material **32**, but at a temperature which does not cause degradation of second material **32**. In another alternative embodiment, second material **32** has a melting point or heat of reaction temperature that is higher than that of first material **31**, but at a temperature which does not cause degradation of first material **31**.

Various examples of golf balls according to the present invention are set forth below.

## EXAMPLE 1

A polybutadiene core **21** having a diameter of about 1.50 to 1.55 inches can be covered with a three-layer cover comprised of the following:

| Material | FIRST MATERIAL 11 SURLYN 7930 | SECOND MATERIAL 21 SURLYN 8320 |
|---|---|---|
| Composition | 30% | 70% |
| Tensile Strength, psi | 3,800 | 3,100 |
| Tensile Strain @ Break, % | 290 | 770 |
| Flexural Modulus, psi | 67,000 | 2,800 |
| Melt Flow, g/10 min | 1.8 | 0.9 |
| Hardness, Shore D | 68 | 25 |
| Bashore Resilienc | 53 | 42 |

* Material properties from supplier's data.

This example can be formed by forming cover hemispheres in a mold. The first and second materials should be heated to approximately 400-425°F and injected into a 40°F mold. The first material will adhere to the surfaces of the mold to form the inner and outer layers of the cover hemisphere and the second material will flow between the inner and outer layers to form an intermediate layer. The two hemispheres can be compression molded about the polybutadiene core to form the inner cover of the ball. The inner cover is preferably formed to an outer diameter of about 1.55 to 1.64 inches.

Then an outer cover comprised of a thermoset urethane such as that described in U.S. Patent Nos. 5,334,673 and 6,210,294 or a polyurea material such as that described in U.S. Patent No. 5,484.870 can be cast over the inner cover layer. These patents are incorporated by reference herein in their entirety.

Preferably, the outer cover has a hardness of about 50 to 65 shore D when measured on the ball. The outer cover material of this example preferably has a flexual modulus of about 5,000 to 30,000 psi.

In an alternate embodiment the first and second materials can be inversed.

**EXAMPLE 2**

A polybutadiene core having a diameter of about 1.50 to 1.55 inches is covered with an inner cover, which is covered by a three-layer outer cover comprised of the following:

| Material | FIRST MATERIAL 11 SURLYN 8320 | SECOND MATERIAL 21 SURLYN 7930 |
|---|---|---|
| Composition | 30% | 70% |
| Tensile Strength, psi | 3,100 | 3,800 |
| Tensile Strain @ Break, % | 770 | 290 |
| Flexural Modulus; psi | 2,800 | 67,000 |
| Melt Flow, g/10 | 0.9 | 1.8 |
| Hardness, Shore D | 25 | 68 |
| Bashore Resilience | 42 | 53 |

*Material properties from supplier's data.

A golf ball core can be covered with an inner cover such as those described in U.S. Patent No. 5,688,191, which is incorporated herein in its entirety. Preferably, an inner cover comprising a dynamically vullcanized thermoplastic elastomer, functionalized styrene-butadiene elastomer, metallocene polymer or blends thereof is formed over the core such that the inner cover has an outer diameter of about 1.55 to 1.62 inches.

This example was formed by first forming cover hemispheres in a mold. The first and second materials were heated to approximately 400°F-425° F and injected into a 40°F. The first material adhered to the surfaces of the mold to form

the inner and outer layers of the cover hemisphere and the second material flowed between the inner and outer layers to form an intermediate layer. The two hemispheres were then compression molded about the inner cover to form the outer cover.

## EXAMPLE 3

A polybutadiene core having a diameter of 1.560 inches can be covered with a thin three layer inner cover of the material composition listed in Example 1 above, and a three layer outer cover of the material composition listed in Example 2 above.

This example was formed by first forming the inner cover hemispheres as described in Example 1 and compression molding them about the polybutadiene core, and then forming the outer cover hemispheres as described in Example 2 and molding them about the inner cover to form a golf ball having a total of 7 layers.

## EXAMPLE 4

A polybutadiene core having a diameter of 1.560 inches is covered with a thin three layer inner cover of the material composition as listed in Example 2 above, and a three layer outer cover of the material composition listed in Example 1 above.

This example can be made by first, forming the inner cover hemispheres, as described in Example 2, and compression molding them about the polybutadiene core. Then forming the outer cover hemispheres as described in Example 1 and molding them about the inner cover to form a golf ball having a total of 7 layers.

The materials Surlyn 7930 and 8320 are registered trademarks of the DuPont Company. The golf balls in the examples were constructed using a compression molding method. However, it will be apparent to those skilled in the art that the golf balls can also be constructed by the retractable pin injection molding process, which involves injection molding of the cover directly around a core positioned on pins. The

pins are removed once the cover material surrounds the core and has solidified to the extent the core will not move. In this process, the compression molding seam **60** can be eliminated. After the cover materials have hardened, the covered core is removed and finished to form a completed golf ball. Based on the teachings herein, the necessary modifications to the standard retractable pin injection molding processes will be readily apparent to those skilled in the art.

Optionally, one or more of the inner layers may serve as moisture barrier layers that will protect against reduced COR values, due to moisture take-up by the core **21**. Preferably one of the intermediate layers **25**, **28** may serve as a moisture barrier layer, more preferably the intermediate layer **25** will serve as the moisture barrier. The use of moisture barriers is described in co-pending Patent Application 09/973,342, which is incorporated by reference herein in its entirety .

A moisture barrier should have a moisture vapor transmission rate that is less than that of the outer cover layer, and more preferably, less than the moisture vapor transmission rate of an ionomer resin such as Surlyn®, which has a rate in the range of about 0.45 to about 0.95 grams per mm/m$^2$ per day. The moisture vapor transmission rate is defined as: the mass of moisture vapor that diffuses into a material of a given thickness per unit area per unit time. The preferred standards of measuring the moisture vapor transmission rate include: ASTM F1249-90 entitled "Standard Test Method for Water Vapor Transmission Rate Through Plastic Film and Sheeting Using a Modulated Infrared Sensor," and ASTM F372-99 entitled "Standard Test Method for Water Vapor Transmission Rate of Flexible Barrier Materials Using an Infrared Detection Technique," among others.

The manipulation of moment of inertia via the filling (or foaming or otherwise reducing specific gravity) of the core **21** and cover layers **24-29** provide the opportunity to further improve upon distance and spin. The low specific gravity core **21** or layers **24-29** can be made from a number of suitable materials, so long as the low specific gravity contributes to the soft compression and resilience of the golf ball. The material can be from a thermosetting syntactic foam with hollow sphere fillers or

microspheres in a polymeric matrix of epoxy, urethane, polyester or any suitable thermosetting binder, where the cured composition has a specific gravity less than 1.1 g/cc and preferably less than 1.0 g/cc. Additionally, any number of foamed or otherwise specific gravity reduced thermoplastic or thermosetting polymer compositions or foaming agents may also be used such as metallocene-catalyzed polymers and blends thereof described in U.S. Patent Nos. 5,824,746 and 6,025,442 which are incorporated by reference herein in their entirety. Further, a thermoset polyurethane composition having a specific gravity or less than 1.3 g/cc such as a nucleated reaction injection molded or cast polyurethane may be used. Such a composition may result in a gas-filled or cellular solid layer.

As discussed in U.S. Patent 5,971,870, which is incorporated by reference herein in its entirety, fillers may be or are typically in a finely divided form. For example, in a size generally less than about 20 mesh, preferably less than about 100 mesh U.S. standard size, except for fibers and flock, which are generally elongated, flock and fiber sizes should be small enough to facilitate processing. Filler particle size will depend upon desired effect, cost, ease of addition, and dusting considerations. The filler preferably is selected from the group consisting of precipitated hydrated silica, clay, talc, asbestos, glass fibers, aramid fibers, mica, calcium metasilicate, barium sulfate, zinc sulfide, lithopone, silicates, silicon carbide, diatomaceous earth, polyvinyl chloride, carbonates, metals, metal alloys, tungsten carbide, metal oxides, metal stearates, particulate carbonaceous materials, micro balloons, and combinations thereof. Non-limiting examples of suitable fillers, their densities, and their preferred uses are as follows:

| Filler Type | Sp. Gr. | Comments |
|---|---|---|
| **Precipitated hydrated silica** | **2.0** | **1, 2** |
| **Clay** | **2.62** | **1, 2** |
| **Talc** | **2.85** | **1, 2** |
| Asbestos | 2.5 | 1, 2 |
| Glass fibers | 2.55 | 1, 2 |
| Aramid fibers (KEVLAR®) | 1.44 | 1, 2 |
| Mica | 2.8 | 1, 2 |
| Calcium metasilicate | 2.9 | 1 ,2 |

| | | |
|---|---|---|
| Barium sulfate | 4.6 | 1, 2 |
| Zinc sulfide | 4.1 | 1, 2 |
| Lithopone | 4.2-4.3 | 1, 2 |
| Silicates | 2.1 | 1, 2 |
| Silicon carbide patelets | 3.18 | 1, 2 |
| Silicon carbide whiskers | 3.2 | 1, 2 |
| Tungsten carbide | 15.6 | 1 |
| Tungsten oxide | 5.8 | 1 |
| Diatomaceous earth | 2.3 | 1, 2 |
| Polyvinyl chloride | 1.41 | 1, 2 |
| **Carbonates** | | |
| Calcium carbonate | 2.71 | 1 ,2 |
| Magnesium carbonate | 2.20 | 1, 2 |
| **Metals and Alloys (powders)** | | |
| Titanium | 4.51 | 1 |
| Tungsten | 19.35 | 1 |
| Aluminum | 2.70 | 1 |
| Bismuth | 9.78 | 1 |
| Nickel | 8.90 | 1 |
| Molybdenum | 10.2 | 1 |
| Iron | 7.86 | 1 |
| Steel | 7.8-7.9 | 1 |
| Lead | 11.4 | 1, 2 |
| Copper | 8.94 | 1 |
| Brass | 8.2-8.4 | 1 |
| Boron | 2.34 | 1 |
| Boron carbide whiskers | 2.52 | 1, 2 |
| Bronze | 8.70-8.74 | 1 |
| Cobalt | 8.92 | 1 |
| Beryllium | 1.84 | 1 |
| Zinc | 7.14 | 1 |
| Tin | 7.31 | 1 |
| **Metal Oxides** | | |
| Zinc oxide | 5.57 | 1, 2 |
| Iron oxide | 5.1 | 1, 2 |
| Aluminum oxide | 4.0 | |
| Titanium oxide | 3.9-4.1 | 1, 2 |
| Magnesium oxide | 3.3-3.5 | 1, 2 |
| Zirconium oxide | 5.73 | 1, 2 |
| **Metal Stearates** | | |
| Zinc stearate | 1.09 | 3, 4 |
| Calcium stearate | 1.03 | 3, 4 |
| Barium stearate | 1.23 | 3, 4 |
| Lithium stearate | 1.01 | 3, 4 |
| Magnesium stearate | 1.03 | 3, 4 |
| **Particulate carbonaceous materials** | | |
| Graphite | 1.5-1.8 | 1, 2 |
| Carbon black | 1.8 | 1, 2 |
| Natural bitumen | 1.2-1.4 | 1, 2 |

| | | |
|---|---|---|
| Cotton flock | 1.3-1.4 | 1, 2 |
| Cellulose flock | 1.15-1.5 | 1, 2 |
| Leather fiber | 1.2-1.4 | 1, 2 |
| **Micro balloons** | | |
| Glass | 0.15-1.1 | 1, 2 |
| Ceramic | 0.2-0.7 | 1, 2 |
| Fly ash | 0.6-0.8 | 1, 2 |
| **Coupling Agents Adhesion Promoters** | | |
| Titanates | 0.95-1.11 | |
| Zirconates | 0.92-1.11 | |
| Silane | 0.95-1.2 | |

1 Particularly useful for adjusting density of the inner cover layer.
2 Particularly useful for adjusting flex modulus of the inner cover layer.

Referring to FIG. 10, golf ball cover hemispheres can also be molded in sandwich injection-molding machine 70 that includes two accumulation chambers 72 and 74 for materials 31 and 32. This sandwich injection-molding machine also includes two mold halves 76 and 78 to form a plurality of mold cavities 80. However, this machine further includes a hot runner system 82 comprised of a hot manifold 84 and hot runners 86 and 88 interconnecting the accumulation chambers 72 and 74 with the mold cavities 80. The hot runners 86 and 88 are maintained at a temperature above the melting point of the materials 31 and 32 so that the material does not solidify therein. A predetermined amount of the first material 31 is fed into the accumulation chamber 72 and injected through the hot runner system 86 into the mold cavities 80. Then a predetermined amount of the second, different material 32 is injected from accumulation chamber 74 through hot runner system 88 and into the mold cavities 80. This eliminates the waist that is created in the cold runner 35 discussed above and creates a quicker molding method.

Foaming agents may manipulate the moment of inertia and provide improvement upon distance and spin. As stated above the co-injection molding may produce a cover of three thin layers utilizing two different materials. The use of dissimilar materials together generates unique properties. A soft outer layer over a hard middle layer can yield a ball having improved spin when the ball is struck by a

club such as a wedge, yet it still can maintain medium spin and excellent velocity when struck by a driver. When used in this way foaming agents reduce the hardness and modulus of the resultant cover.

In a co-injected molded cover of this invention, as best seen on FIG. 2, foaming agents when used in the middle layer improve feel and change the moment of inertia, and when they are used in the inner and outer layers they increase spin and control moment of inertia.

Co-injection molding having a foamed layer allows for a multitude of variations regarding spin, moment of inertia and velocity. Examples of possible combinations include: very thin inner and outer layers (0.005” to 0.015”) over a thick or thin foamed middle layer; thick inner and outer layers over a thin inner layer; and each layer having the same thickness. These different thicknesses of polymers can be made by a multitude of materials, such as hard SURLYN® over and under soft, foamed non-ionomeric materials; or foamed SURLYNS® over and under hard resilient ionomer. The foamed cover layer can be used over a solid, one-piece core; a solid, dual core; or a wound ball (with a solid or liquid center). The co-injection molded cover could also combine different groups of thermoplastic materials such as: ionomers, block copolymers, non-ionomers, thermoplastic urethanes, and metallocenes, and blends of those materials. These materials may also be loaded with gravity adjusting materials to improve moment of inertia.

Golf balls were made and test conducted to determine how a golf ball cover would be affected by the introduction of a foaming agent into the composition of the cover material. The covers were made using varying blends of SURLYN® and FUSABOND® which are available from DuPont, and the foaming agent ACTIVEX 535, available from Boehringer Ingelheim Chemicals, Petersburg, Virginia.

Six different blends of material for golf ball covers were made and tested. The results appear in the following Tables.

**"40 HOUR" DATA**

| Blend No. | Density (g/cm³) | Flex Modulus (ksi) [act hrs] | Tensile Modulus (ksi) [act hrs] | Stress @ Yield (ksi) | Strain @ Yield (%) | Stress @ Break (ksi) | Strain @ Break (%) |
|---|---|---|---|---|---|---|---|
| 1 | 0.942 | 54.3(1.2) [49.25] | 41.35 (4.25) | 2.13 (0.11) | 17.68 (1.67) | 2.86 (1.310) | 152.7 (20.3) |
| 2 | 0.942 | 53.8(1.4) [48] | 38.57 (4.09) | 2.19 (0.10) | 15.33 (0.67) | 2.64 (0.06) | 138.9 (13.5) |
| 3 | 0.948 | 51.6(0.9) [47.75] | 38.57 (4.09) | 2.19 (0.10) | 17.14 (1.94) | 3.22 (0.15) | 192.0 (11.7) |
| 4 | 0.933 | 37.4(1.3) [46.5] | 26.22 (2.24) | 1.91 (0.01) | 17.24 (1.65) | 2.69 (0.02) | 201.3 (15.6) |
| 5 | 0.936 | 35.7(1.3) [37.5] | 24.28 (1.07) | 1.83 (0.03) | 17.70 (1.33) | 2.73 (0.22) | 187.5 (10.9) |
| 6 | 0.940 | 35.9(1.0) [39] | 27.77 (2.74) | 1.93 (0.01) | 16.37 (1.19) | 2.84 (0.68) | 188.8 (6.9) |

**2 WEEK DATA**

| Blend No. | % Activex 535 | Flex Modulus (ksi) | Tensile Modulus (ksi) | Stress @ Yield (ksi) | Strain @ Yield (ksi) | Stress @ Break (ksi) | Strain @ Break (%) |
|---|---|---|---|---|---|---|---|
| 1 | 0 | 60.74 (0.39) | 56.46 (11.94) | 2.47 (0.02) | 11.33 (0.55) | 2.30 (0.15) | 155.8 (15.3) |
| 2 | 1 | 58.66 (1.01) | 42.87 (4.53) | 2.43 (0.02) | 12.88 (0.40) | 2.48 (0.06) | 163.1 (7.7) |
| 3 | 3 | 56.61 (0.71) | 38.51 (5.23) | 2.36 (0.02) | 13.18 (0.68) | 2.97 (0.05) | 205.2 (13.1) |
| 4 | 0 | 40.99 (0.34) | 29.37 (4.69) | 1.82 (0.02) | 18.59 (2.09) | 2.39 (0.03) | 211.2 (11.3) |
| 5 | 1 | 40.47 (0.30) | 26.79 (2.84) | 1.80 (0.01) | 19.13 (3.64) | 2.24 (0.53) | 219.6 (28.4) |
| 6 | 3 | 40.05 (0.30) | 25.41 (2.65) | 1.80 (0.02) | 19.27 (2.76) | 2.32 (0.15) | 216.5 (12.4) |

The blends were comprised of the following materials:

(1) 50% SURLYN 7940® and 50% SURLYN 8940®;

(2) 49.5% 7940®, 49.5% 8940®, and 1% Activex 535®;

(3) 48.5% 7940®, 48.5% 8940®, and 3% Activex 535®.

(4) 35% 7940®, 45% 8945®, 20%, and Fusabend 525D®;

(5) 35% 7940®, 44% 8945®, 20% 525D® and 1% Activex 535®; and

(6) 35% 7940®, 42% 8945®, 20% 525D® and 3% Activex 535®.

It is fairly apparent that the introduction of a foaming agent into the composition of the cover material significantly lowers the flex and tensile moduli and also the stress yield of the ball.

While it is apparent that the illustrative embodiments of the invention herein disclosed fulfills the objectives stated above, it will be appreciated that numerous modifications and other embodiments may be devised by those skilled in the art. Therefore, it will be understood that the appended claims are intended to cover all such modifications and embodiments which come within the spirit and scope of the present invention.